Thermal Emission Measurements (5-25 μm) of Hawaiian Palagonitic Soils With Implications for Mars; Ted L. Roush¹ and James F. Bell III², ¹San Francisco State Univ. and NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035-1000, ²NRC/NASA Ames Research Center, MS 245-3, Moffett Field CA 94035-1000

Background: There is ample evidence that abundant iron-bearing minerals are present on Mars. This evidence takes the form of in situ analyses [1-4], previous and continuing Earth-based telescopic spectroscopic observations [e.g. 5,6], Viking Lander and Orbiter multispectral imaging [7-10], and Phobos-2 multispectral imaging [11,12]. Information regarding the crystalline or amorphous nature of the iron-bearing (and other) surface materials on Mars can provide insight into the availability of liquid water at the surface and the duration, mode, and extent of weathering.

Data from Viking X-ray fluorescence analyses, magnetic experiments, and aerosol imaging were interpreted as indicating the presence of a variety of iron-rich materials, including iron oxides [1-4,13]. However, since the Viking Landers did not carry any instruments capable of determining mineralogy, the exact mineralogical form of the iron-bearing material remains uncertain.

Interpretations of continuing visual, near-, mid- and far-infrared spectroscopic observations of Mars from the Earth and spacecraft over the past 20 years have revealed that the ferric mineralogy occurs in two distinct forms: (1) nanophase or truly amorphous Fe^{3+} -bearing materials [14,15] that spectrally resemble certain terrestrial palagonites [e.g. 16-20]; and (2) well-crystalline ferric oxides like hematite $(\alpha-Fe_2O_3)$, maghemite $(\gamma-Fe_2O_3)$, or magnetite (Fe_3O_4) [1,13,15, 21-24]. The available data indicate that the poorly-crystalline "palagonite-like" phases are spectrally dominant [e.g. 5,6] and that the well crystalline ferric oxides cannot constitute an abundance of more than about 4-8 wt. % [24].

The research presented here represents the initial phase of a broader project that is intended to provide data in the mid- and far-infrared spectral region for both well-characterized iron oxides/oxyhydroxides and poorly crystalline or amorphous materials (e.g. palagonites). Such information can be used in the interpretation of past and future thermal infrared observations of Mars.

Spectral Studies: In the middle infrared (5-25 μ m), spectral features arise from vibrational motions of atoms and molecules which compose the materials. These fundamental modes are much more intense than any associated combination and/or overtones of these modes and hence remote sensing observations in the infrared are extremely sensitive to minor concentrations of these absorbing species [25].

Careful laboratory studies have shown that the coloring agent in certain Mars analog Hawaiian palagonitic soils is nanophase iron oxide [18,19,26]. We have measured the emissivity of two Mauna Kea palagonitic soils whose transmission spectra exhibit different spectral features [27] and of a thermally-altered volcanic tephra sample that exhibits a wide range of crystallinity and degree of alteration (from black cinders to fully hematitic) [19]. Both of these samples may represent analogs for formation mechanisms involving the production of highly-altered secondary weathering products on Mars. The emission spectra of all samples were measured at the TES spectroscopy laboratory [28] at Arizona State University with the cooperation of Dr. Phil Christensen. The data were converted to emissivity using blackbody measurements combined with measurements of each sample at different temperatures [29].

Results: Emissivity spectra for coarse and fine particle size separates of each sample are shown in Figure 1. Several trends are immediately obvious. First, the finer particle size fractions exhibit increasingly lower emissivity than the coarser sizes at wavenumbers above 1400 cm⁻¹. This effect may be a manifestation of the increased importance of multiple scattering at these frequencies rather than Fresnel-like reflections at lower frequencies. Second, emissivity peaks in the 1000-1400 cm⁻¹ region in the fine fraction samples are shifted to higher frequencies relative to the same feature in the coarse fraction samples. This may be a particle size effect, or it may be due to variations in the silicate and/or iron-bearing mineralogy between the coarse and fine samples [e.g., 19]. While we do not make specific mineralogic assignments for the various spectral features seen in these data, we note that a broad

emissivity peak possibly due to silicates is present near 1200-1300 cm⁻¹ and that narrower features near 1400-1600 cm⁻¹ and near 400 cm⁻¹ are possibly consistent with crystalline iron oxide minerals like hematite and/or goethite [30,31].

This preliminary study has demonstrated that naturally-occurring palagonites, thought to be good visible to near-IR spectral analogs for Mars, exhibit complex emissivity spectra at thermal wavelengths. Disentangling the various spectral signatures that make up the emissivity spectra of these complex assemblages may prove quite important in the interpretation of mid-IR Mars data sets.

References: [1] R.B. Hargraves et al. (1977) JGR, 82, 4547. [2] P. Toulmin et al. (1977) JGR, 82, 4625. [3] B.C. Clark et al. (1977) JGR, 82, 4577. [4] B.C. Clark et al. (1982) JGR, 87, 10059. [5] L.A. Soderblom (1992) in Mars (H.H. Kieffer et al., eds.), 557. [6] T.L. Roush et al. (1993) in Remote Geochemical Analysis (C. Pieters and P. Englert, eds), 367. [7] L.A. Soderblom et al. (1978) Icarus, 34, 446. [8] T.B. McCord et al. (1982) JGR, 87, 10129. [9] J.B. Adams et al. (1986) JGR, 91, Soderblom et al. (1978) Icarus, 34, 446. [8] T.B. McCord et al. (1982) JGR, 87, 10129. [9] J.B. Adams et al. (1986) JGR, 91, Soderblom et al. (1978) Icarus, 34, 446. [8] T.B. McCord et al. (1982) JGR, 87, 10129. [9] J.B. Adams et al. (1980) JGR, 94, 1573. [11] S. Murchie et al. (1993) Icarus, in press. [12] J.F. Mustard et al. (1993) JGR, 98, 3387. [13] J.B. Pollack et al. (1977) JGR, 82, 4479. [14] R.V. Morris and H.V. Lauer Jr. (1990) JGR, 95, 10159. [17] D.L. Evans and J.B. Singer et al. (1979) JGR, 87, 10159. [17] D.L. Evans and J.B. Adams (1980) PLPSC 11, 757. [18] R.V. Morris et al. (1990) JGR, 95, 14427. [19] J.F. Bell III et al. (1993) JGR, 98, 3373. [20] A. Banin (1992) LPI Tech. Rpt. 92-04, 1. [21] R.V. Morris et al. (1985) JGR, 90, 3126. [22] J.F. Bell III et al. (1990) JGR, 14447. [23] R.B. Hargraves et al. (1979) JGR, 84, 8379. [24] J.F. Bell III (1992) Icarus, 100, 575. [25] J.F. Bell III and 95, 14447. [23] R.B. Hargraves et al. (1979) JGR, 84, 8379. [24] J.F. Bell III (1992) Icarus, 100, 575. [25] J.F. Bell III and 95, 14447. [23] R.B. Hargraves et al. (1979) JGR, 84, 8379. [24] J.F. Bell III (1992) Icarus, 100, 575. [25] J.F. Bell III and 95, 14447. [23] R.B. Hargraves et al. (1979) JGR, 84, 8379. [24] J.F. Bell III (1992) Icarus, 100, 575. [25] J.F. Bell III and 95, 14447. [23] R.B. Hargraves et al. (1979) JGR, 84, 8379. [24] J.F. Bell III (1992) Icarus, 100, 575. [25] J.F. Bell III and 95, 14447. [23] R.B. Hargraves et al. (1979) JGR, 84, 8379. [24] J.F. Bell III (1992) Icarus, 100, 575. [25] J.F. Bell III

Acknowledgements: This research is supported by funding from: Mars Observer Participating Scientist Program; NASA's Geology and Geophysics Program via RTOP 151-01-60-01 and NAGW 2212; and from NASA's Exobiology program via RTOP 185-52-62-07.

Figure 1. Emissivity spectra of Hawaiian palagonitic samples PH-1 (a thermally altered palagonitic tephra from Mauna Kea) and 91-1 (a palagonitic tephra from South Point, island of Hawaii). Both coarse and fine size fraction spectra are shown. Arrows indicate subtle shifts in emissivity peak position between the two particle size regimes shown. The vertical line shows the frequency of the strong H-O-H bending fundamental caused by molecular water associated with these samples.

